Things of science

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CRYSTAL GROWTH

Unit No. 338

CRYSTAL GROWTH

This unit of THINGS of science contains five different chemicals with which you can grow crystals: potassium alum, Epsom salt, Rochelle salt, manganese chloride and borax.

The beauty of gem stones and other crystals has never ceased to fascinate man. Equally as fascinating as the outward appearance of crystals is their inner structure and how they become what they are. Scientists still do not know exactly how a crystal takes shape, although there are theories as to what happens, and research is still continuing in this age-old field.

Precious gems form only a small part of the crystal world. Salt, sugar and metals, and most other solids are crystalline in structure. Some crystals may be made up of individual molecules and others owe their structure to a lattice arrangement of ions, or charged atoms. Sugar is a molecular crystal, while table salt and the crystals you will be making from the materials in this unit are ionic crystals.

It took thousands of years to form many of the natural crystals found in the earth's crust. Heat, pressure and the changing environment through the years

provided the conditions for the formation of the stones you see displayed in museums.

The crystals you will produce will take much less time to grow, from a few hours to a few days in most cases. But this is because you will be supplying the necessary materials and the proper environment. In nature crystals can grow only when the right materials happen to be present when conditions happen to be right.

The way in which crystals grow, whether in nature or in the laboratory, is basically the same. Crystals start growing from a central nucleus which may be a group of molecules or atoms of the substance or perhaps a speck of dust. Individual particles of the substance attach themselves one by one, and in orderly fashion, to the nucleus, causing it to increase in size outwardly. The resultant orderly structure is the distinguishing feature of all crystalline solids. The smallest part of the structure that bears all the characteristics of the substance and determines the final shape of the crystal, whether molecular or ionic, is called the unit cell.

All crystals are polyhedra. That is, they are solids bounded by plane faces. There

are six basic crystal systems in which all crystals form:

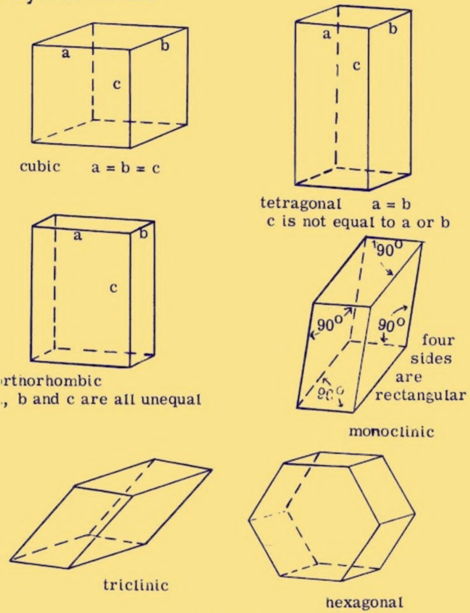

Fig. 1

cubic—all edges are equal and all their angles are 90°.

tetragonal—all angles are again, 90°, but the crystal is larger or shorter in one direction than in the other two.

orthorhombic—all angles are 90°, but the length in each of the three directions is different.

monoclinic—sixteen of the angles are 90°; the other eight are either greater or less than 90°.

triclinic—no angles are right angles.

hexagonal—six-sided prism.

All these shapes will not be represented by the crystals made from the specimens in this unit, but as you continue your investigations in crystallography further and work with a variety of chemicals, you will be able to select materials to include all these systems.

Crystals may be grown in the laboratory by several methods—from gas, molten material or a solution. In the experiments here you will grow crystals from solutions.

SATURATED AND SUPERSATURATED SOLUTIONS

A solution consists of two parts: the solvent, usually a liquid, in which a substance is dissolved and a solute, usually a solid, which is dissolved in the solvent. Only a certain amount of any substance will dissolve in a given quantity of water at a given temperature. When a solvent dissolves as much as it can of

a solute and will accept no more, the solution is said to be saturated.

After a solution is saturated at room temperature, it can usually be made to dissolve more solute by heating. When the solution is cooled to room temperature again, it will usually retain the extra solute, at least for a while. The solution is then said to be supersaturated. Some supersaturated solutions retain the excess solute longer than others, but all supersaturated solutions are unstable and a slight jolt or the addition of a grain of the original substance can cause the excess solute to crystallize out. We make use of this property of supersaturated solutions to produce crystals in the laboratory.

BEGINNING PREPARATIONS

First identify your specimens.

POTASSIUM ALUM—In bag #1—Potassium aluminum sulfate, $KAl(SO_4)_2 \cdot 12H_2O$; white.

MAGNESIUM SULFATE—In bag #2—Epsom salt, $MgSO_4 \cdot 7H_2O$; clear crystals.

ROCHELLE SALT—In bag #3—Potassium sodium tartrate tetrahydrate, $KNaC_4H_4O_6 \cdot 4H_2O$; white.

MANGANESE CHLORIDE—In plain bag—Anhydrous manganous chloride, $MnCl_2$; pink.

BORAX—In plain bag—Sodium tetraborate, decahydrate, $Na_2B_4O_7 \cdot 10H_2O$; white.

The chemicals included in this unit are non-toxic and additional amounts can be readily obtained from the local drugstore or a chemical company. However, chemicals should always be treated with care. Do not rub your eyes or face or put your fingers in your mouth while working with chemicals and be sure to wash your hands after you finish your experiments.

Next, assemble kitchen type measuring spoons, preferably plastic; a glass stirring rod or a few plastic or uncolored wooden toothpicks for mixing the solutions; about half a dozen shallow flat bottomed glass dishes having a base diameter of two inches or less—small beakers or glass custard cups are excellent for this purpose; small covered jars to store your crystals; and forceps or a small plastic picnic fork to lift out the crystals from the solutions. Be sure all the containers and equipment are clean and dry.

Tap water may be used for making the crystals, but distilled water will give

better results because it is free of impurities.

Have at hand a small pan containing an inch or so of water for warming the solutions.

Because the saturation point of a solution varies with temperature, grow your crystals in an area where there is little temperature change. A sudden drop in temperature could cause a cascade of many small crystals that may ruin any larger crystal that is forming, while an increase in temperature could cause a growing crystal to be redissolved.

POTASSIUM ALUM

Crystals can be grown very easily from potassium aluminum sulfate, $KAl(SO_4)_2 \cdot 12H_2O$, or potassium alum.

Note that the formula shows that there are 12 molecules of water attached to the potassium aluminum sulfate. These molecules of water are known as water of hydration and are essential for the crystalline structure of potassium alum. Many other crystals contain water of hydration. A later experiment will show what happens to the crystal if the water is removed.

Experiment 1. Place one level teaspoon of the potassium alum in one of your glass dishes. Add to this three tea-

spoons of water one at a time being careful not to splash it up against the sides of the dish. Stir the mixture to dissolve the solute. If all of it dissolves, add more potassium alum in ¼-teaspoon quantities until no more will dissolve. The solution is then saturated.

Place the dish in a pan of hot water. Stir the solution to dissolve the excess remaining at the bottom of the dish. After this has dissolved add another ¼-teaspoon of the alum to be sure you will obtain a supersaturated solution.

Wrap and cover the dish with a cloth or towel and place it in a spot where it will remain undisturbed and where temperatures are fairly constant. The cloth prevents too rapid cooling of the solution and slows evaporation. At the same time it protects the solution from dust.

Examine the solution after it has cooled to room temperature. Note that the excess solute remains in solution. You have produced a supersaturated solution of the potassium alum.

Experiment 2. Allow the supersaturated solution to stand undisturbed for several hours or overnight. Do you see any crystals at the bottom of the dish? You may find two or more large crystals about ¼-inch or more in size.

If a mass of small crystals has settled out of your supersaturated solution, your solution was probably too concentrated. Remove some of the solid and redissolve the remaining crystals by placing the dish in hot water again. Allow the solution to cool in a protected area as before.

If after two days, no crystals have formed, drop a grain or two of the original potassium alum into the solution. Crystals should form after several hours. If you still do not get crystals and the material you added has disappeared, then your solution is not saturated. Add more alum a very small amount at a time until no more will dissolve. Heat the solution to dissolve the excess and then allow it to cool as before.

Because crystal formation depends upon the chance formation of a nucleus, you will find, as you experiment, that similar preparations of solutions do not always produce the same results. Two similar solutions may not necessarily form crystals at the same temperature. However, once a crystal forms, it will grow continuously until all the excess material has come out of solution.

Note the shape of the crystals, Are they octahedral?

Crystals grown at the bottom of a con-

tainer are always distorted because the face resting on the bottom cannot grow, while the other faces continue to grow. Your alum crystal therefore may acquire a hexagonal or triangular shape.

If you have more than one crystal, note that they are similar in shape but are not exactly alike. This is because the faces of crystals grow at different rates and the rates are modified by the environmental conditions.

Potassium alum crystals when perfectly formed are colorless and either cubic or octahedral in shape. The ideal alum crystal starts as a cube and finally emerges as an octahedron (Fig. 2).

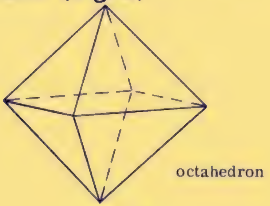

Fig. 2

But, crystal growth is influenced by many factors including the presence of impurities and temperature changes and rarely does a crystal show the ideal structure.

Experiment 3. Lift out your largest

potassium alum crystal carefully and place it on a soft cloth or absorbent paper. Dry it. Turn it over and examine the underside—the side that was against the bottom of the dish—with a magnifying glass.

Is there a slight depression in the center? Note that the hollow is shaped somewhat like a shallow inverted pyramid and comes to a point at the center of the crystal. Can you see the striations parallel to the sides? They indicate the growth of the crystal along the edges. As the material is deposited and the sides of the crystal grow, they are gradually lifted up. However, the solution cannot reach the center to deposit new material, causing the hollow to form.

Experiment 4. Are your crystals clear or are they somewhat cloudy? If crystals grow too rapidly, they will appear milky. The slower the crystals grow the more transparent they will be.

When a crystal grows too fast, open spaces are left between the layers of molecules or ions since they do not have time to be stacked closely against each other in their proper orientation before a new layer of material forms over the vacancies sealing them off permanently. The open spaces remain filled with the solution and when the rays of light strike the crystal,

they are scattered by these holes causing the crystal to appear white.

If a crystal grows sufficiently slowly, the material is packed more uniformly and fewer spaces occur; those that do occur are smaller. When light strikes the crystal, the small spaces do not scatter the rays so much and the crystal appears clear.

Therefore, in order to obtain clear crystals you should allow your solutions to cool and evaporate slowly.

Experiment 5. Even if some of the crystals are cloudy, there may be others in the solution that are clear. Remove any well-formed crystals an eighth of an inch or larger. Dry them and place them in a covered jar and label it.

Do you find any crystals that have grown together? Observe these under a magnifying glass and note how the edges that are in contact may have become deformed.

Select two or three crytsals for further growth. Place these in a clean dish and pour the solution (now saturated rather than supersaturated since the excess solute has crystallized out) over them leaving other crystals at the bottom of the dish behind.

Since the quantities you are working

with are small, you will not want to waste any solution. Therefore, when pouring the solution from one container to another, place a stirring rod or a long toothpick across the lip of the dish to direct the flow (Fig. 3). Practice this with plain water first so that you will not spill the solution. Pouring the liquid portion off solids that have settled out of a solution is called decanting.

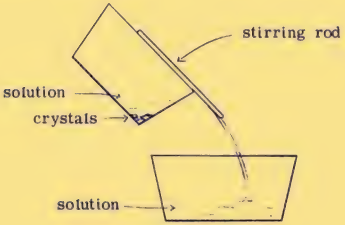

Fig. 3

After decanting, don't discard the excess crystals. They can be reused. Store them in a jar for use as seeds later or use them to make more solution.

Cover the dish containing the growing crystals with a cloth to prevent evaporation from taking place too rapidly. As evaporation takes place, the solution becomes slightly supersaturated and the ex-

cess solute is deposited on the crystals. Watch them as they grow from day to day.

If many small crystals also form, transfer the larger crystals into another dish and decant the solution over them. The tiny crystals will also grow and retard the growth of the large crystals.

Experiment 6. The crystalline form of many compounds depends upon the water of hydration. Potassium alum contains 12 molecules of water of hydration. The water molecules arrange themselves in a definite way around the ions in the crystal lattice and always assume the same pattern.

Place one of your crystals of potassium alum in a dish exposing it to the air. If the air is very dry, it will soon lose some of its water and turn cloudy.

Take another crystal and place it on a piece of aluminum foil in a frying pan. Heat the pan very slowly and note what happens to the crystal. You may be surprised at the quantity of water released by the heated crystal.

Continue to warm the crystal until the water is completely evaporated. What does your crystal look like now? Its crystalline structure has been completely destroyed by the removal of the water.

Experiment 7. Some crystals lose water and others attract water when exposed to the atmosphere. A crystal that gives up moisture to the air is said to be efflorescent and one that absorbs moisture from the air is said to be deliquescent or hygroscopic.

Since most water soluble crystals react in one of these two ways to the atmosphere you should spray them with a clear plastic spray or paint them with fingernail polish if you wish to keep them permanently. This seals them and prevents them from absorbing moisture or losing it.

Don't spray all your specimens. You will need a few for later experiments.

Save your saturated solution for growing a larger crystal.

GROWING LARGER CRYSTALS

You have seen how easy it is to grow crystals in a dish by evaporation. However, although such crystals are attractive, they are distorted as you have observed. To produce larger and better formed crystals, it is necessary to allow them to grow unobstructed and freely in all directions.

Experiment 8. First gather together small transparent vials, such as cylindrical pill bottles, some paper clips or fine wire, and sewing thead.

Select a well-shaped crystal from among

those you have just made. Be sure it is a single crystal so that the final product will also be a single crystal. The crystal should be about ⅛- to ¼-inch in size. Sometimes a crystal will dissolve a little when first placed in a solution, even if the solution has been saturated because a rise in temperature has occurred. If the crystal is too small you may lose it.

Tie a thread six or more inches long around the crystal using a slip knot (Fig. 4).

Open up a paper clip or bend a piece

Fig. 4

of fine wire to suspend the thread (Fig. 5).

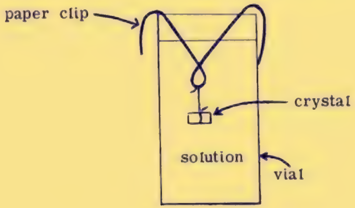

Fig. 5

Tie the thread to the wire, adjusting its length so that the crystal will hang about

midway down into the solution.

Fill the vial almost full with a saturated solution of potassium alum. Use your original solution. Make additional saturated solution if necessary by first making a slightly supersaturated solution of the potassium alum and then allowing the excess solute to crystallize out.

Lower the crystal into the solution. Do not let the crystal rest against the side of the container or its growth will be hindered at the point of contact. The crystal and thread should be completely submerged. If the thread extends above the surface, it will act like a wick and the solution will travel up the thread and may deposit crystals on it as it evaporates.

Place the vial in a protected place and cover it lightly with a cloth so that evaporation will take place slowly. Watch the crystal grow from day to day. As the solution evaporates and its height in the vial decreases add fresh saturated solution. You may also wish, from time to time, to transfer the crystal to a vial of fresh saturated solution.

Do not throw away the old solution or any crystals that may have settled at the bottom of the vial. They can be reused to make more saturated solution.

Experiment 9. Look carefully at the

shape of the growing crystal. Does it show a tendency to form an octahedron?

After you have obtained a crystal of the desired size, remove it from the solution and dry it. Spray it with plastic and store it in a covered container on a piece of cotton or soft cloth to prevent injury to the crystal surface.

Experiment 10. Your crystal may not be a perfect octahedron. But do not be discouraged. Most crystals grown in the home or laboratory are irregular because of the many influences affecting their growth. No two crystals you grow will be exactly alike, even if the solutions are made in the same way since each crystal will be exposed to slightly different conditions.

Your specimen, even if irregular, will give you an idea of how crystals grow.

Experiment 11. Observe the faces on the crystal. Note how smooth they are. What are their shapes?

Note the angles formed by any two faces. The angles are always the same for a crystal of a particular substance, no matter how large or small it is, or how irregular the crystal may be. This constancy of angles is a characteristic of all crystals and helps crystallographers identify them. The angles are measured by an instru-

ment called a goniometer.

Experiment 12. Is your crystal equally developed on all sides?

Crystals may grow unequally if the solute is not distributed evenly throughout the solution. Also, as a crystal grows and removes material from the surrounding solution, the region around it becomes less concentrated. The less concentrated portion is less dense and rises creating a current known as the density or convection current. This, too, contributes to irregular growth.

If many crystals settle at the bottom of the container, the solution is more concentrated there and the lower portion of the crystal may show greater growth.

Experiment 13. Find an irregular seed crystal and allow it to grow. Note the interesting structure you obtain.

To grow crystals from the other chemicals in this unit, follow the same methods you used to produce the potassium alum crystals.

MAGNESIUM SULFATE

Magnesium sulfate, $MgSO_4 \cdot 7H_2O$ or Epsom salt, is very soluble in water.

Experiment 14. To make the solution, place two level teaspoons of the magnesium sulfate in a dish and then add two teaspoons of water. Mix gently to

dissolve the salt. When completely dissolved, add more salt, a half a teaspoon at a time. When no more will dissolve, place the dish in hot water to dissolve the excess. Then add another ¼ teaspoon of the salt to be sure the solution will be supersaturated. Heat until the solution is clear and all particles have disappeared. Wrap the container in a cloth and place it in a portected place.

Watch for crystals to form.

Experiment 15. Note that the magnesium sulfate crystals are needle-like prisms, quite different in shape from the potassium alum crystals. Examine them on all sides with a magnifying glass. Are the crystals orthorhombic? The crystals should be clear and transparent.

Experiment 16. Perform the same experiments with these crystals as you did with the potassium alum crystals. Compare your results.

Experiment 17. Select one of the crystals as a seed to grow a larger crystal. When growing your larger specimen of magnesium sulfate, note that crystals tend to form at the surface of the solution as evaporation takes place. Some of the crystals may drop down into the solution and on the large crystal you are growing. If they remain there, they will start new

growths on the surface of the crystal. To help prevent this, transfer the solution and crystal each day to a fresh container.

Experiment 18. Compare this crystal with the potassium alum crystal. In which direction does the magnesium sulfate crystal grow fastest?

Note its prismatic structure. Allow the light to play on it and you will see a beautiful rainbow of colors.

ROCHELLE SALT

Rochelle salt or potassium sodium tartrate, $KNaC_4H_4O_6 \cdot 4H_2O$, like magnesium sulfate, is very soluble in water.

Experiment 19. To make your solution, place two level teaspoons of Rochelle salt in a dish and gradually add two teaspoons of water, stirring to dissolve the solute. After the salt is completely dissolved, add more, a half a teaspoon at a time, until no more will dissolve. Place the dish in a pan of hot water and then add another half teaspoon of the salt to make a slightly supersaturated solution. Be sure the salt is completely dissolved and the solution clear.

The solubility of Rochelle salt is especially sensitive to temperature changes. Store the solution in a safe place with the container wrapped in a cloth.

You may get large flat crystals or long

hexagonal prisms similar to the Epsom salt crystals. They should be absolutely clear.

Experiment 20. As the crystals grow, they usually broaden, assuming a rectangular shape.

Examine the underside of a large flat crystal. Do you see a hollow?

Perfect Rochelle salt crystals are rhombic. A rhombus has parallel sides with equal opposite angles. Is this true of any of your crystals?

Experiment 21. Rochelle salt crystals grow fairly rapidly. Allow a crystal to grow for several days at the bottom of the dish. Observe the crystal shape from the side. Does it look like half a hexagon?

Crystals that are grown at the bottom of a container often look like a well-formed crystal with part of the structure removed.

Experiment 22. Suspend a crystal of Rochelle salt in a saturated solution and grow a large specimen.

What shape crystal do you obtain? Is it monoclinic? Compare it with the specimens grown at the bottom of the dish.

MANGANESE CHLORIDE

The pink compound in the unmarked bag is manganese chloride, also called manganous chloride. This chemical is an-

hydrous, that is, it contains no water of hydration. If it is exposed to humid air for an extended period of time it will absorb water from the atmosphere.

When anhydrous manganese chloride is dissolved in water it becomes hydrated. That is, water molecules attach themselves to the positive manganese ion, four molecules to each ion. When it crystallizes from the solution the ions remain hydrated and the crystals that are formed are composed of manganese chloride tetrahydrate, $MnCl_2 \cdot 4H_2O$.

Experiment 23. Place two level teaspoons of the manganese chloride in a dish and then add two teaspoons of water. Stir the mixture gently to dissolve the flakes. If the flakes are completely dissolved, add more, ¼ teaspoon at a time. When the solution is saturated, place the dish in hot water to dissolve any remaining flakes. Add another half teaspoon of the substance and dissolve it completely. Wrap the container in a cloth and allow it to cool.

The crystals may not form for about two days.

The manganese chloride solution may contain a brownish suspension, an impurity that is very difficult to remove in the manufacture of this chemical. How-

ever, it will not interfere with crystal growth.

Decant your solution leaving as much of the brown residue behind as possible and follow the same procedure as before to grow your crystals. After the solution has been decanted several times, it will become fairly clear.

Examine the specimens you obtain. What color are they? What is their shape? Are they monoclinic?

Store the crystals in a tightly covered jar. Manganese chloride crystals are very hygroscopic and if left in the open air quickly attract moisture and become sticky.

Experiment 24. Make a little more saturated solution, decanting it to clear it, and suspend a crystal in the solution. The crystal will grow slowly.

What is its shape? How does it compare with the specimens grown at the bottom of the dish?

SODIUM BORATE

Sodium borate, $Na_2B_4O_7 \cdot 10H_2O$, or sodium tetraborate, is also known as borax. It is less soluble than the other chemicals in this unit.

Experiment 25. Place ¼ teaspoon of the sodium borate in a dish and add three teaspoons of water. Add a little more borax if it dissolves completely. Place the

dish in hot water to dissolve the excess and then add just a very small amount to make a slightly supersaturated solution. Proceed in the same way as you did with the other materials to form your crystals.

Compare the rate of growth of the borax crystals with your other specimens.

Larger crystals of borax may be a little more difficult to grow. What is the shape of the crystals? Borax belongs to the monoclinic system of crystals.

Experiment 26. Allow a few of the small crystals to stand in the open air for several days. What happens to them? Borax is highly efflorescent and the crystals turn to a white powder when exposed to the atmosphere.

UNDER THE MICROSCOPE

If you have a microscope you can watch a crystal grow using only moderate magnification.

Experiment 27. Make a small quantity (about one teaspoonful) of highly supersaturated solution of potassium alum. Place a drop of the warm supersaturated solution on a slide and place a coverglass over it.

Watch the slide carefully. As the solution cools, the excess solute will begin to crystallize. Note how rapidly the crystal grows.

CRYSTAL GROWING IN WATER GLASS

There is still another method for growing crystals which will allow them to grow freely without the use of a thread.

This method uses water glass, or sodium silicate, available in drug stores, that is gelled with acid. The crystals are grown from a solution, and as they form they remain suspended in the gel. The system used by Dr. John L. Torgesen and H. Steffen Peiser of the National Bureau of Standards is described in *Chemistry* magazine for September 1965, p. 15, published by the American Chemical Society, Washington, D.C.

The technique is simple and produces undistorted crystals. It should provide you with many hours of interesting research in crystallography.

If you wish to make crystals of other materials than those in this unit, select them with care. Metallic salts produce the most colorful specimens, but they are usually harmful and many are deadly poisons. As a precaution, check first with a chemist or other scientist before purchasing any chemicals you may wish to experiment with.

For those of you who wish to pursue

the subject further here are a few references:

Elementary chemistry textbooks.

Crystals, Charles Bunn, Academic Paperbacks, New York, 1965.

Crystals and Crystal Growing, Alan Holden and Phylis Singer, Doubleday & Company, Garden City, New York, 1960.

Crystals and Light, Elizabeth A. Wood, D. Van Nostrand Company, Princeton, N. J., 1964.

The Nature of Solids, Alan Holden, Columbia University Press, New York, 1968.

Appreciation is expressed to Dr. John L. Torgesen, National Bureau of Standards, Washington, D. C., for reviewing this booklet.

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